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Mass transport in CuInSe₂ from first principles

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The wide scatter in experimental results has not allowed drawing solid conclusions on self-diffusion in the chalcopyrite CuInSe₂ (CIS). In this work, the defect-assisted mass transport mechanisms operating in CIS are clarified using first-principles calculations. We present how the stoichiometry of the material and temperature affect the dominant diffusion mechanisms. The most mobile species in CIS is shown to be copper, whose migration proceeds either via copper vacancies or interstitials. Both of these mass-mediating agents exist in the material abundantly and face rather low migration barriers (1.09 and 0.20 eV, respectively). Depending on chemical conditions, selenium mass transport relies either solely on Se dumbbells, which diffuse with a barrier of 0.22 eV, or also on Se vacancies whose diffusion is hindered by a migration barrier of 2.19 eV. Surprisingly, indium plays no role in long-range mass transport in CIS; instead, indium vacancies and interstitials participate in mechanisms that promote the formation of antisites on the cation sublattice. Our results help to understand how compositional inhomogeneities arise in CIS.

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Keywords: Copper indium diselenide, Point defects, Diffusion, Density-functional theory

I. INTRODUCTION

CuInSe₂ (CIS) and its quaternary analog, CuIn_xGa_{1-x}Se₂ (CIGS), have gained a foothold as absorber materials in thin-film solar cell technology. Meanwhile, the defect physics of CIS continues to puzzle researchers, and much effort has been spent on characterizing and identifying its defect structure (for a review, see e.g.¹). Point defects in CIS play an essential role not only by influencing directly the electronic properties of the material, but also through mediating diffusion during material growth, processing, and device operation. Knowledge of these atomic-scale processes would greatly benefit device control and performance, yet no solid conclusions on the topic have been reached. Even in silicon, one of the simplest materials, the dominant diffusion mechanisms were debated for decades [ref?]. It is not surprising, then, that a material with a much more complicated structure such as CIS poses an even greater challenge for characterization.

The diffusion phenomena occurring in chalcopyrite thin-film structures have been explored experimentally by measuring concentration profiles with methods such as secondary-ion mass spectroscopy (SIMS)²⁻⁴, Auger electron spectroscopy (AES)⁵, radioactive tracer technique (RTT)⁶⁻⁸, and nuclear magnetic resonance (NMR)⁹. However, extracting quantitative measures regarding self-diffusion from the experiments has proven a challenging task, and the studies can at most raise speculations of the dominant self-diffusion mechanisms in CIS: copper and indium diffusion have mostly been attributed to a vacancy-driven mechanism^{2,3,5,30}, while selenium-related evidence is pointing towards an interstitial mechanism⁶.

Results should always be interpreted taking into account the limitations imposed by the methodology used. Indirect methods like SIMS and AES provide values for chemical diffusion coefficients, which by definition are affected by the presence of internal and external electric fields¹⁰. While direct methods such as RTT and NMR can be used to obtain actual self-diffusion coefficients, the data gathered so far is **both** too scarce and shows significant scatter to allow drawing solid conclusions on the mass transport mechanisms in CIS. The scatter in the data reflects in part differences in sample composition, conductivity¹¹, and experimental conditions. Different self-diffusion mechanisms may also operate in distinct temperature regimes, further complicating the interpretation of the results.

In order to fill the gap in our knowledge regarding self-diffusion in CIS, the diffusion phenomena can be approached from a computational perspective. First-principles simulations offer the possibility to examine viable migration paths and mechanisms atom-wise and quantify their corresponding contributions to mass transport. A few copper-related reports on the topic have recently been published^{17,18}, but they treat the diffusion of copper vacancies and interstitials separately and do not state conditions under which each mechanism would dominate. In the present work, we will go more in depth to the topic than previous studies, considering all three components of CIS. We use first-principles calculations to answer the following questions regarding mass transport in CIS: (1) **What is the most probable mobile species?** (2) **How does the dominant mass transport mechanism for each component depend on the stoichiometry of the material and on the temperature?**

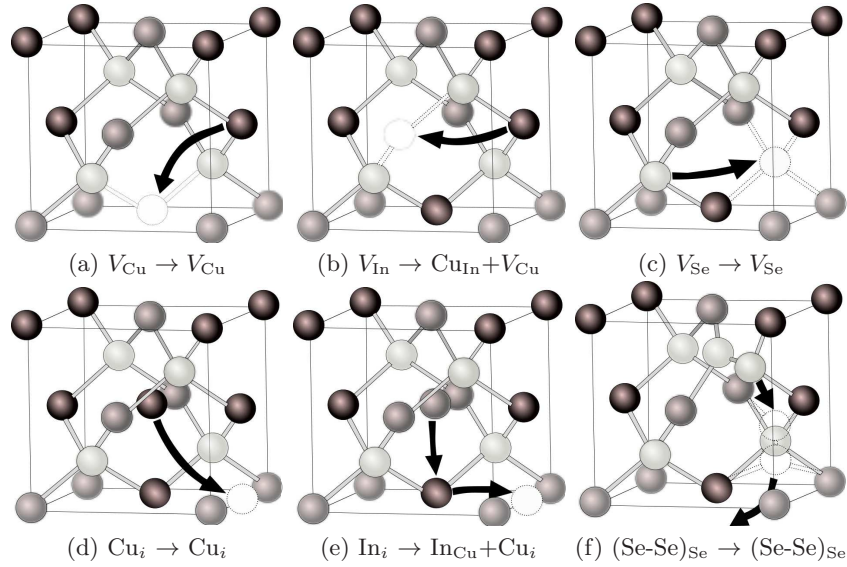


FIG. 1. Schematic diagram of the most favorable migration path for each considered defect. The copper atoms are drawn in dark color, indium atoms in grey, and selenium atoms in light color. Only one-eighth of the 64-atom supercell is shown for clarity.

II. METHODOLOGY

A. Defining diffusion parameters

Atomic diffusion or mass transport encompasses all diffusion by one atomic species in a compound, namely, all atoms exchanging places belong to the same species. Yet making diffusion jumps requires assistance from point defects. A defect-mediated diffusion jump typically proceeds by the exchange of an atom with a vacancy (vacancy-mediated diffusion) or by an atomic jump through interstitial space in the lattice (interstitial-mediated diffusion). For instance, in order for vacancy-mediated diffusion to occur, the diffusing atom must meet a vacancy and overcome an activation barrier, E_m , that separates it from the vacant lattice site. After the jump, the atom waits for another vacancy in order to make the next jump. The corresponding contribution to the self-diffusion coefficient is then the product of the vacancy concentration, C_V , and the vacancy diffusivity, $D_V \sim \exp(-E_m/kT)$, describing the probability to jump. Similarly, the contribution from interstitial-mediated diffusion is $C_I D_I$, where C_I is the concentration of interstitials and D_I is their diffusivity. The total self-diffusion coefficient of an atomic species is the sum of all these different mechanisms i : $D_{\text{self}} = \sum_i C_i D_i$.

Defect concentrations C_i are sensitive to the experimental conditions. Under thermal equilibrium conditions, a defect concentration is described by the Arrhenius equation, being proportional to $\exp(-E_f/kT)$, where E_f is the formation energy of the defect¹⁹. If the samples are held long enough at a certain temperature, they are expected to reach thermal equilibrium, and the defect

concentrations will equilibrate accordingly – this is the case in the experimental studies that are referred to in this article. In thermal equilibrium, an activation energy of

$$E_a = E_m + E_f \quad (1)$$

is then required for atomic diffusion to take place. Theoretically calculated values for E_a can be compared to experimental values derived from the slope of an Arrhenius plot of self-diffusion coefficients measured in different temperatures. It should be noted that, under nonequilibrium conditions such as during irradiation or ion implantation, the defect concentrations C_i stay independent of temperature and Eq. 1 is reduced to the form $E_a = E_m$.

The dominant mass transport mechanism for each elemental component can vary depending on the stoichiometry of the material (through E_f) as well as temperature. In each compositional regime, the main mass transport mechanism is determined by the one having the lowest activation energy. The temperature dependence of the transport mechanisms is revealed through their self-diffusion coefficients. The mechanism with the largest self-diffusion coefficient dominates in a certain temperature range.

B. Computational details

The calculations in this work have been performed using the plane-wave code VASP^{12,13} with the projector-augmented wave (PAW) method^{14,15}. The plane-wave basis set has been truncated with a cut-off energy of 400 eV. The exchange-correlation potential has been

modelled with the range-separated hybrid functional HSE06¹⁶, which has shown considerable improvement over (semi)local functionals in the description of the atomic and electronic properties of CIS^{17,18,20}. The portion of Hartree-Fock exchange, α , has been set to the value of 0.25 derived from theory²¹.

The formation energies E_f for each mass-mediating agent have been computed following the procedure outlined in our previous work²⁰, including finite-size scaling^{22,23}. Each defect has been considered in its relevant charge state^{20,32}. The formation energies are sensitive to the stoichiometry of the material and, in the case of charged defects, also to the Fermi level position μ_e .

The energetically most favorable migration route has been identified out of the different possible paths for each mass-mediating agent (details of the other possible paths will be described elsewhere²⁶). The activation barriers, E_m , for the reaction paths have been computed employing the climbing-image nudged-elastic-band method (CINEB)²⁴ in a 64-atom supercell with a k point sampling of $2 \times 2 \times 2$. The structures have been allowed to relax until the forces on each atom fell below 0.01 eV/Å. It should be noted that the value of E_m does not depend on the stoichiometry, but is simply the difference in energy between the equilibrium and saddle-point configurations. As such, it appears to converge much faster with supercell size than mere formation energies. Additional calculations involving supercells of 144 atoms indicate that barrier values vary at most by 0.07 eV, suggesting that a 64-atom supercell is sufficient for this purpose. After the evaluation of the barriers, the self-diffusion coefficients $D(\mu_e, T)$ have been estimated as described in²⁵.

III. RESULTS AND DISCUSSION

A. Copper mass transport

CIS is typically grown Cu-poor, with an even more Cu-poor layer forming on top of the samples⁷. The copper deficiency is believed to result in an abundance of copper vacancies. This expectation is supported by the remarkably low formation energy computed for V_{Cu} in several prior theoretical works, including ours^{17,20,27,28}. According to our results, copper vacancies prefer to diffuse in the copper sublattice of the chalcopyrite structure with a migration barrier of 1.09 eV. The corresponding mechanism is illustrated in Figure 1(a).

Copper interstitials may co-exist with copper vacancies in the material, and they populate the octahedral sites in the lattice especially under excess Cu conditions. As presented in Table I, they have the lowest formation energy among the three intrinsic interstitials in CIS. A copper interstitial diffuses from one octahedral site to the next equivalent one with a migration barrier of only 0.20 eV.

While both V_{Cu} and Cu_i can mediate mass transport in CIS, one of them will dominate depending on con-

ditions such as stoichiometry and temperature. Comparing the activation energies of the two mechanisms at different Fermi level positions in Figure 2, it is seen that copper interstitials are the leading mediating agents for copper throughout the Fermi level range under Cu-rich conditions. Under Cu-poor conditions, copper interstitials mediate mass transport up to Fermi level position of 0.2 eV (i.e. p -type material) after which copper vacancies will prevail until pinning prevents the Fermi level from rising any further²⁹. The impact of the two mechanisms can also be compared as a function of temperature by plotting the dependency of the corresponding self-diffusion coefficients (not shown). In the case of copper, the curves do not cross, i.e. a transition from one mechanism to another does not occur in typical growth and processing temperatures, thus leaving copper mass transport dependent only on the Fermi level position.

Experimentally determined values for the activation energies of copper have been published on several occasions, ranging from 0.2 to 1.25 eV (see¹⁷ and references therein). Yet as explained in the detailed analysis in¹⁰, these values mostly do not represent self-diffusion, and actual data on self-diffusion is too limited to provide a reliable value for the activation energy. The migration barrier values for copper computed in this work agree closely with the previous HSE06 calculations^{17,18}.

Evidence supporting interstitial-driven copper transport has been accumulating little by little. From the experimental side, copper vacancies were suspected for a long time to mediate copper diffusion based on indirect evidence of presumed vacancy concentrations correlating with diffusion coefficients³⁰. However, the experimentally determined diffusion coefficients showed such a large scatter that it started to seem like only one diffusion mechanism would not be able to account for it all. Besides vacancies, it was suggested that another mechanism such as interstitials could be operational at least under Cu-rich conditions⁷. Only recently, the feasibility of Cu_i migration was demonstrated by theoretical calculations¹⁸, which we now confirm and extend with an explicit analysis of the effect of chemical conditions and temperature.

B. Selenium mass transport

Selenium defects exist predominantly in the neutral charge state and therefore maintain a constant formation energy almost throughout the Fermi level range²⁰. Selenium vacancies form particularly easily under Se-poor conditions with a formation energy of 1.04 eV²⁰. However, the low formation energy is counterbalanced by a high migration energy of 2.19 eV, which effectively prevents their diffusion. Such a large value probably stems from the strong lattice relaxation around V_{Se} : the two nearest-neighbor In atoms around the vacant site form a dimer bond^{20,31} that must be broken before diffusion can occur. The migration jump of V_{Se} is shown schematically

in Figure 1(c).

Extra selenium atoms are accommodated as dumbbells in the CIS lattice. A dumbbell consists of two selenium atoms sharing the same lattice site (see Ref.³²) and can be oriented in multiple ways. Dumbbells dissociate if one of the two Se atoms jumps away. In practice, the jumping atom will end up sharing a lattice site with another Se atom, thus forming yet another dumbbell configuration as depicted in Figure 1(f). These jumps require only 0.22 eV, indicating that extra Se atoms will be quite mobile.

Comparing the activation energies of the two mechanisms in Figure 2, selenium diffusion via dumbbells is without doubt energetically more favorable than via vacancies under Se-rich conditions. Under Se-poor conditions, however, the mechanisms have similar activation energies and therefore both can be expected to contribute to mass transport. The preferred mechanism does not depend on temperature.

Our results are in line with radioactive tracer measurements which indicate that selenium diffusion occurs via neutral selenium interstitials⁶. The study was conducted in single-crystal CIS when the Se₂ partial pressure was varied at a high temperature. Single-crystal samples are better suited for comparison with theoretical results than polycrystalline material, which is usually dominated by grain boundary processes. Indeed, in another RTT measurement probing polycrystalline material, the prevalent self-diffusion mechanism for selenium was suspected to be grain boundary diffusion at least in the temperature range of 200-400°C⁸. The activation energy obtained for Se grain boundary diffusion was only 0.26 eV, while that for lattice diffusion was estimated to be 1.98 eV. The estimated value was derived from limited data from a previous study employing junction-depth measurements³³ and lies somewhat lower than what has been obtained

in our study. Based on these considerations, selenium mass transport probably occurs via grain boundaries in polycrystalline material and, depending on chemical conditions, either via selenium vacancies or dumbbells in single-crystal material.

C. Indium mass transport

Indium vacancies and interstitials are not likely to exist in CIS samples in significant quantities based on thermodynamic considerations. Their formation energies depend strongly on the Fermi level position due to their high charge states (3− for V_{In}, 3+ for In_i), and are generally large apart from small, specific regions of stoichiometry and Fermi level position³⁴.

Indium diffusion via indium vacancies or interstitials is hampered by antisite formation. For instance, V_{In} would rather jump to the nearest-neighbor copper site and thus form an antisite Cu_{In} (migration barrier of 0.70 eV) than to exchange places with an indium atom (1.00 eV). The corresponding path is shown schematically in Figure 1(b). Since the final configuration of the lowest-energy jump, Cu_{In}+V_{Cu}, is rather loosely bound with a binding energy of only 0.09 eV, V_{Cu} can be expected to move away from the Cu_{In} antisite and continue diffusing on its own. Reversing the initial reaction is somewhat less likely due to a barrier of 1.21 eV and would still not result in mass transport.

In_i never jumps to another interstitial site, but instead heads straight to a copper site. As a result, an In_{Cu} antisite is formed, and the copper atom is kicked out into an interstitial site (Figure 1(e)). The energy gain from the jump to the Cu site is so large (1.21 eV) that all extra In atoms can be expected to eventually end up in the Cu sublattice. This will add to the already significant concentration of In_{Cu} antisites that will be created due to their exceptionally low formation energy³⁵, which we confirm. The binding energy of the In_{Cu}+Cu_i complex is 0.08 eV, meaning that Cu_i can quite easily detach from the antisite and start diffusing on its own. If In_{Cu} would encounter a copper vacancy, it would be able to take isolated jumps in the copper sublattice, but the impact of this mechanism would be quite negligible on the whole. Based on these results, it can be concluded that neither indium vacancies nor interstitials will contribute to long-range mass transport in CIS.

Experimental investigations of the mobility of indium have often been carried out concurrently with gallium²⁻⁵. These two cannot be practically disentangled in a compound such as CIGS where the cation-III-atoms compete for the same sublattice positions. In and Ga diffusion has been suggested to proceed in the cation sublattice via vacancies again due to variations in diffusivity with respect to the composition of the sample^{2,3,5}. Interestingly, the activation energy for the interdiffusion of indium in single-crystal material has only been recorded in CuGaSe₂ (0.32 eV⁴) but not in CIS. This experimental

TABLE I. Energy barriers of the most favorable migration paths (E_m) and formation energies (E_f) for the vacancies and interstitials in CIS. The formation energies correspond to the initial configuration before the reaction at Fermi level position equal to 0 eV. The formation energies as well as their error bars have been derived using finite-size scaling as described in our previous work²⁰. The error bars also apply to the formation energies under Cu-rich conditions.

	Reaction		Charge state	E_m (eV)	E_f (eV)	
	Initial	Final			Cu-poor	Cu-rich
<i>Vacancy-mediated</i>						
(a)	V_{Cu}	V_{Cu}	1−	1.09	0.64±0.15	1.43
(b)	V_{In}	$\text{Cu}_{\text{In}}+V_{\text{Cu}}$	3−	0.70	3.95±0.80	5.59
	$\text{Cu}_{\text{In}}+V_{\text{Cu}}$	V_{In}		1.21		
(c)	V_{Se}	V_{Se}	0	2.19	2.25±0.10	1.04
<i>Interstitial-mediated</i>						
(d)	Cu_i	Cu_i	1+	0.20	1.09±0.10	0.30
(e)	In_i	$\text{In}_{\text{Cu}}+\text{Cu}_i$	3+	0.28	2.95±0.40	1.31
	$\text{In}_{\text{Cu}}+\text{Cu}_i$	In_i		1.48		
(f)	$(\text{Se-Se})_{\text{Se}}$	$(\text{Se-Se})_{\text{Se}}$	0	0.22	2.15±0.10	3.36

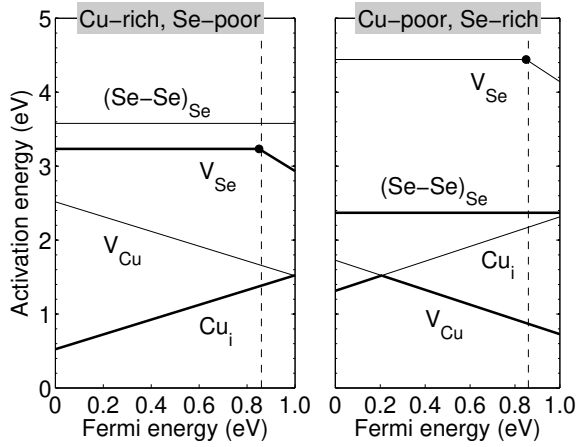


FIG. 2. Activation energies of the **mass transport**-mediating defects in CIS under Cu-rich/Se-poor and Cu-poor/Se-rich conditions. The dominant mass transport mechanism at each value of the Fermi level is determined by the lowest corresponding activation energy, which has been drawn in a thicker line. The dashed vertical line represents the band gap value obtained from the calculations.

evidence together with our computational results leave room for the possibility that In could behave differently in the absence of gallium, and this should be investigated further. Indium diffusion may also be governed solely by grain boundary processes in polycrystalline material, evidence for which was obtained in Ref.^{4,36} in the temperature range of 200-400°C.

IV. CONCLUSIONS

In this work, the mass transport of the three constituents in CIS has been investigated with first-principles calculations. Based on thermal activation energies, copper is found to be the fastest diffusing element in the material, followed by selenium. In contrast, indium will practically not move at all. These results support early experimental observations employing nuclear magnetic resonance spectroscopy (NMR)⁹ and electron-beam-induced current (EBIC)³⁷ which identified copper as the most mobile species out of the two cations in CIS at 300-350°C. At the same time, no mobility of In was observed⁹.

Copper mass transport is mediated by either copper vacancies or interstitials depending on chemical conditions. Both mediating agents exist abundantly in the material and face rather low migration barriers (1.09 and 0.20 eV, respectively). Copper interstitials mediate mass transport under Cu-rich conditions. Under Cu-poor conditions, mass transport occurs via interstitials up to Fermi level position of 0.2 eV, and via copper vacancies at higher electron doping levels. The leading mechanism will remain the same in typical growth and processing

temperatures.

Selenium mass transport also is sensitive to the stoichiometry of the material. Selenium vacancies require only 1.04 eV to form under Se-poor conditions, but their diffusion is hindered by a migration barrier of 2.19 eV. Extra selenium atoms are accommodated as dumbbells in the selenium sublattice and diffuse with a low barrier of 0.22 eV. Under Se-rich conditions, mass transport proceeds via dumbbells, while a competition between the two mechanisms takes place under Se-deficient conditions. Again, the preferred mechanism does not depend on temperature.

Indium mass transport is hampered by antisite formation. Due to their high formation energies, indium vacancies and interstitials would only occur in small concentrations in CIS. Additionally, it turns out that both of them prefer to occupy a copper site. Therefore, they cannot contribute to long-range mass transport.

Out of the considered defects, V_{Cu} , Cu_i , and Se dumbbell diffuse particularly easily in CIS due to their low migration barriers. Instead of staying isolated, they are likely to meet other defects and form clusters, or diffuse out of the samples, as well as heal radiation damages by recombination. As a result of their diffusion, compositional inhomogeneities may arise. Our results help to explain why and how CIS maintains a certain kind of microstructure. This study provides a framework for further studies of defect kinetics in CIS.

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